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Equilibrium Studies of Zinc Ions Removal from Aqueous Solutions by Adsorption on Natural Zeolite

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Abstract: The aim of this study is to use natural zeolite (clinoptilolite) as an adsorbent for the removal of zinc ions from synthetic aqueous solutions. In order to determine the zinc uptake at equilibrium a series of experiments were performed under batch conditions from ion solutions. Experiments were carried out at different initial concentracion of zinc ions and at different initial pH values at 20± 1°C. The adsorption isotherm of the zinc ions on the adsorbent was determined and correlated with the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm exhibited a better fit for the adsorption data than the Freundlich isotherm.

Key words: Zinc ions, adsorption, zeolite, equilibrium.

1. Introduction

Heavy metals are a common pollutant found in various industrial effluents. They are often encountered in metal plating facilities, electroplating, mining operations, fertilizers, battery manufacture, dyestuff, chemical pharmaceutical, electronic device manufactures and many others. Most of heavy metals are highly toxic and are non-biodegradable, therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards.

Removal of these heavy metals can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption, adsorption, etc. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon, clay minerals, biomaterials, industrial solid wastes and zeolites [1].

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^{+}, K^{+}, Ca^{2+} or Mg^{2+}). Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g., lead, nickel, zinc, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal wastewaters, electroplating effluents and agricultural wastewaters [2].

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The aim of this work was to investigate the adsorption of zinc ions onto a natural zeolite (clinoptilolite) whereby the main parameters were the adsorption isotherms parameters.

2. Experiments

2.1 Adsorbent

The natural zeolite-clinoptilolite was used in the recent study as an adsorbent for adsorption of heavy metals, such as zinc. The particle size range of the natural zeolite used in this study was 0.8 to 2.5 mm.

The chemical compositions of natural zeolite are presented in Table 1.

X-Ray Difractometer 6,100 from Shimadzu was used to investigate the mineralogical structure of natural zeolite samples. This technique is based on observing the scattering intensity of an X-Ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The diffraction data obtained are compared to the database maintained by the International Centre for Diffraction Data, in order to identify the material in the solid samples. The results of XRD (Fig. 1) show that the natural zeolite contained clinoptilolite in the majority.

The surface morphology of natural zeolite was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with a Inca 250 EDS system. EDS, stands for EnergyDispersive Spectroscopy, it is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X-Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

Micrographs of natural zeolite samples obtained from SEM analysis are given in Fig. 2. The micrographs clearly show a number of macro-pores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Fig. 3) and the elemental composition of natural zeolite (clinoptilolite) are presented in Table 2.

Results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were K^+ and Ca^{2+}.

2.2 Adsorbate

The heavy metal, Zn, was used as adsorbate in the recent investigations. Synthetic single component solutions of Zn^{2+} were prepared by dissolving a weighed mass of the analytical grade salt $ZnSO_4 \cdot 7H_2O$ in 1,000mL distilled water.

2.3 Experimental Procedure

Adsorption of zinc ions on zeolite was performed with synthetic single ion solutions of Zn^{2+}ions with different initial concentration. Initial pH of prepared

Table 1 Chemical composition of zeolite samples.

Typical chemical composition in % wt			
SiO_2	69.68	CaO	2.01
Al_2O_3	11.40	Na_2O	0.62
TiO_2	0.15	K_2O	2.90
Fe_2O_3	0.93	H_2O	13.24
MgO	0.87	P_2O_5	0.02
MnO	0.08	ratio Si/Al	4.0-5.2
Cation exchange per cation		K^+ 41 meq/100 g Na^+ 16.10 meq/100 g Ca^{2+}67.14meq/100 g Mg^{2+} 3.88 meq/100 g	
Total cation exchange capacity		1.8-2.2 meq/g	

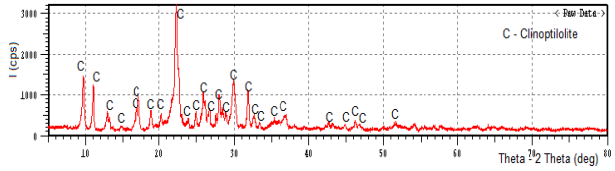


Fig. 1 X-Ray diffraction of natural zeolite.

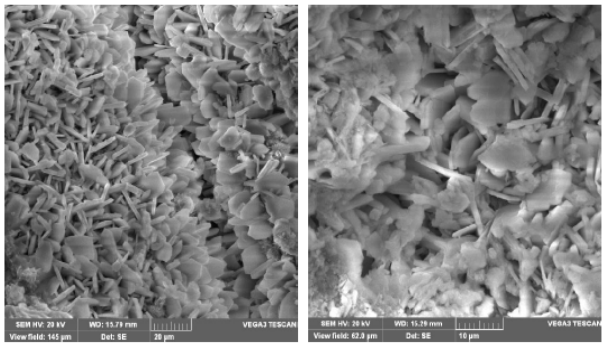


Fig. 2 Micrographs of natural zeolite samples obtained from SEM analysis.

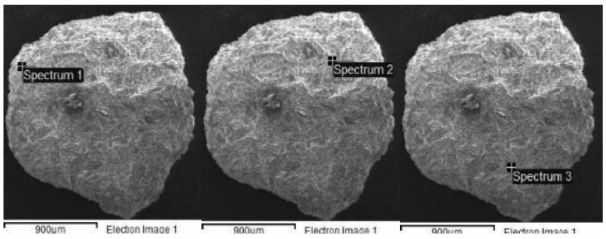


Fig. 3 EDS analysis showing the scanning method for natural zeolite.

solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of zeolite with a certain volume of Zn^{2+} ions solution. Zeolite sample and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 360 min. At the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. The final pH value was also measured. All experiments were performed at room temperature on 20 ± 1 °C. The initial and remaining concentrations of metal ions were determined by Liberty 110, ICP Emission Spectrometer, Varian. Inductively coupled plasma atomic emission spectroscopy(ICP-AES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopythat uses the inductively coupled plasmato produce excited atoms and ions that emitelectromagnetic radiationat wavelengths characteristic of a particularrelement. The intensity of this emission is indicative of the concentration of the element within the sample.

Based on material balance, the adsorption capacity was calculated by using the following expression [3]:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad \text{(mg/g)} \qquad (1)$$

where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and final metal ion concentrations (mg/L), respectivly, V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$\text{AD\%} = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \qquad (2)$$

2.4 Equilibrium Studies

Equilibrium studies generally involve the determination of the adsorption capacity of a given material. This determination is important in accessing

Table 2 EDS analysis showing the elemental composition for natural zeolite (%).

Element	Spect 1	Spect 2	Spect3	Average	Std. deviation
O	58.46	55.4	58.83	57.56	1.882
Na	0.27	0.15	0.3	0.24	0.079
Mg	0.72	0.66	0.77	0.72	0.055
Al	5.28	5.52	5.03	5.28	0.245
Si	29.55	31.36	29.47	30.13	1.068
K	2.73	2.96	2.44	2.71	0.26
Ca	1.9	2.42	1.66	1.99	0.388
Fe	1.1	1.53	1.5	1.38	0.24
Total	100	100	100	100	

the potential of the material as an economic and commercially viable adsorber.

Upon contacting an amount of adsorbent with a solution containing an adsorbable substance adsorption will take place. Adsorption will continue until equilibrium will be established between the substance in solution and the same substance in the adsorbed state. At equilibrium a relationship exists between the concentration of the species in solution and the "concentration" of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent) [4].

Experimental data were also fitted to conventional adsorption mathematical models, namely the Freundlich and Langmuir models. These were used to predict the adsorption performance of natural zeolite. The performance of natural zeolite was also assessed at different initial solution pH levels.

2.4.1 Langmuir Model

The Langmuir isotherm model [5], based on monolayer coverage of adsorbent surfaces by the adsorbate at specific homogeneous sites within the adsorbent, is represented as:

$$q_e = \frac{q_m K_l C_e}{1+K_l C_e} \quad (3)$$

where q_e, mg/g, is the amount of solute adsorbed per unit mass of adsorbent at equilibrium; C_e, mg/L, is the residual adsorbate concentration in solution at equilibrium; q_m, mg/g, is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites, K_l, L/mg, is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute, which is evaluated through linearization of Eq. (3):

$$\frac{1}{q_e} = \frac{1}{k_l q_m C_e} + \frac{1}{q_m} \quad (4)$$

2.4.2 Freundlich Model

The Freundlich isotherm model, based on multilayer adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat, is represented as:

$$q_e = k_f C_e^{1/n} \quad (5)$$

where, k_f and n are empirical Freundlich constants that are dependent on experimental conditions. k_f is an indicator of adsorption capacity, while n is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation, given by:

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \quad (6)$$

1/n is the heterogeneity factor; values of 1/n << 1 indicate heterogeneous adsorbents, while values closer to or even 1 indicate a material with relatively homogeneous binding sites [6]. Natural zeolite should be a heterogeneous adsorbent due to its porous nature. Alvarez-Ayuso et al. [7], Avila [8] and Gunay et al. [9] successfully used the Freundlich adsorption isotherm to model their results from equilibrium experiments.

3. Results and Discussion

The main objective of the equilibrium studies was to determine the maximum capacity of natural zeolite towards zinc removal under the studied conditions.

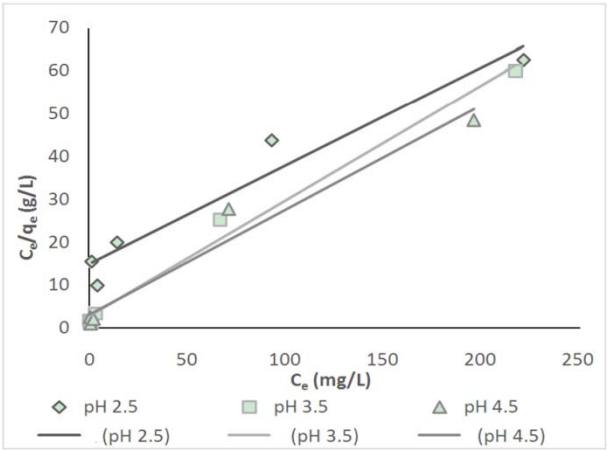
In order to carry out the equilibrium studies, 5 g of natural zeolite was mixed with 100 mL solution of the zinc cations at different initial pH levels (2.5, 3.5 and 4.5) and concentrations (5, 25, 50, 200 and 400 mg/L), and agitated for 360 min. The results of equilibrium studies for zinc cation are presented in Table 3 and Figs. 4-6.

The highest experimental amount of zinc removed, $q_{e\,max}$, was 4.1 mg/g, from a solution whose initial pH was 4.5 and the amount of zinc removed from solution increased with an increase in initial solution pH.

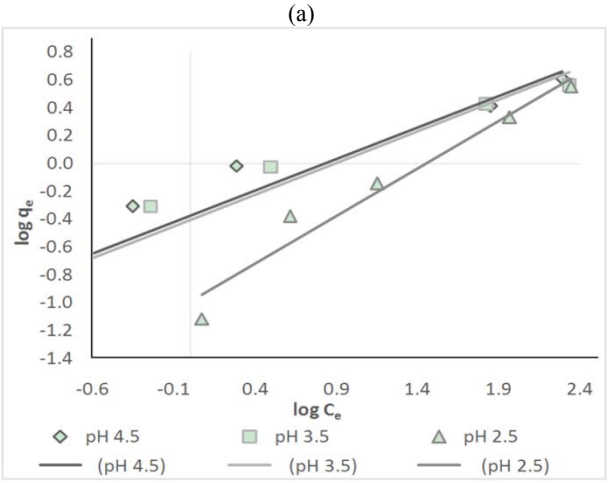
This is mainly due to the fact that at high metal concentrations, there is a higher solute concentration gradient, and this provides the necessary driving force for metal ions to displace exchangeable cations on the surface and from the internal micro-pores of natural zeolite [10-12]. However, this increasing trend is valid up to a point at which the maximum capacity of the natural zeolite samples for the respective heavy metal cation is achieved, that is, its saturation point.

Table 3 Calculated equilibrium adsorption isotherm constants for the uptake of zinc from solution by natural zeolite.

pH	Experimental		Langmuir				Freundlich			
	q_e (mg/g)	C_e (mg/L)	q_m (mg/g)	K_l (L/mg)	R^2	R_L	K_f (L/mg)	$1/n$	N (g/L)	R^2
2.5	3.556	222.19	4.3937	0.0151	0.9463	0.142	0.1021	0.6812	1.4680	0.9561
3.5	3.6392	218.04	3.7272	0.0968	0.99	0.025	0.3934	0.4545	2.2002	0.9111
4.5	4.065	196.75	4.1085	0.0785	0.9626	0.031	0.4211	0.4517	2.2139	0.8566



(a)

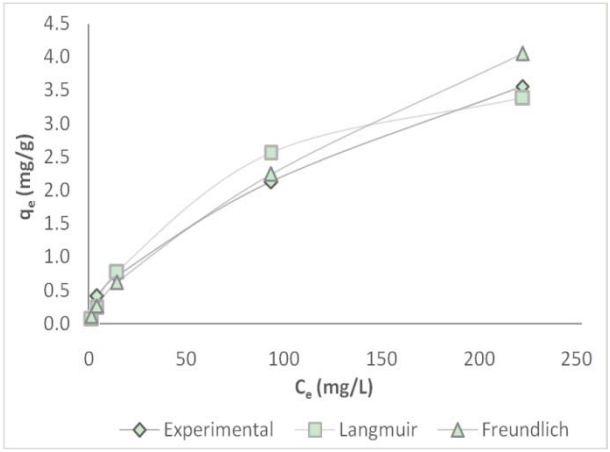


(b)

Fig. 4 Adsorption isotherms (a) Langmuir isotherms and (b) Freundlich isotherms.

Experimental data obtained from equilibrium experiments were fitted to the Langmuir and Freundlich adsorption isotherms.

The values of the constants in the models and correlation coefficients obtained are summarized in Table 3 and the data calculated by theoretical models (lines) are shown in Figs. 4 and 5. According Freundlich model, values of the heterogeneity factor *1/n*, indicate that natural zeolite is hetero gene ousadsorbent. Based on the correlation coefficients (R^2)



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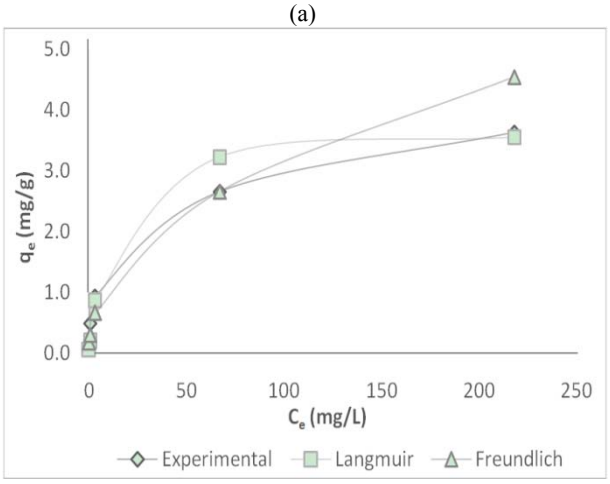

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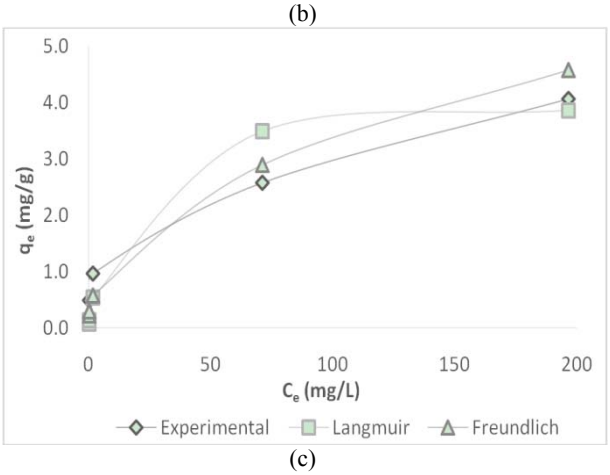


(c)

Fig. 5 Equilibrium isotherms for the removal of zinc from solution(a) pH 2.5 (b) pH 3.5 and (c) pH 4.5.

shown in Table 3, the adsorption isotherms for different initial pH values of solutions can be best described by the Langmuir model. The applicability of the Langmuir isotherm suggests monolayer coverage of the Zn^{2+} at the surface of the natural zeolite or that a similar exchangeable ions with equivalent concentration was exchanged by Zn^{2+}.

The essential characteristics of Langmuir isotherm can be described by a dimensionless constant called equilibrium parameter, R_L, which is usually defined by:

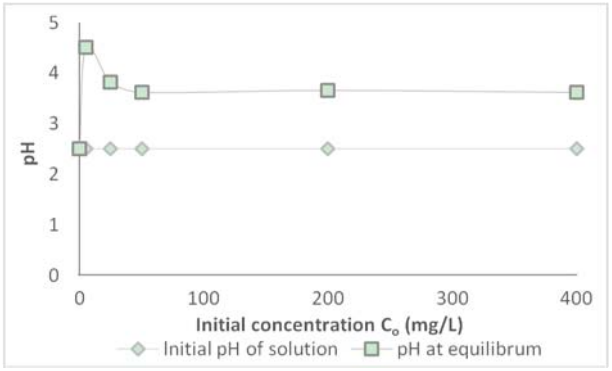
$$R_L = \frac{1}{(1+K_l+C_0)} \quad (7)$$

where, C_0 is the highest initial Cu^{2+} concentration (mg/L) and K_l is the Langmuir constant that indicates the nature of adsorption. The value of R_L indicates the type of the adsorption isotherm to be either unfavourable (R_L> 1), linear (R_L = 1), favourable (0 <R_L< 1) or irreversible (R_L = 0).

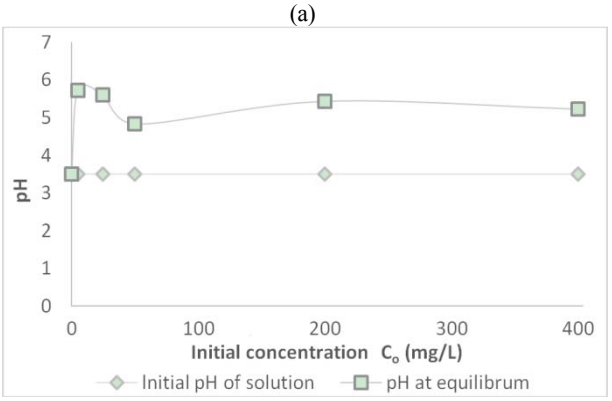
The R_L values reported in Table 3, show that the behaviour of Zn^{2+} adsorption for all different pH values was favourable (0 <R_L< 1).

Fig. 5 also show the adsorption capacity of natural zeolite for zinc at different initial solution pH levels. It can be observed that there is a general increase in adsorption capacity as the solution pH increases. This is mainly attributed to the decrease in H+ ion concentration as the initial pH level increases from 2.5 to 4.5. H^+ ions act as competitors for available adsorption sites on the natural zeolite surface, and hence at low pH levels, H^+ ions are more concentrated and thus because of the concentration driving force will be adsorbed in preference to zinc ions, resulting in lower adsorption capacities for zinc ions [7]. Similar results are obtained by Motsi [12]. The adsorption capacity increases from pH 2.5 to 5.7, but the Freundlich isotherm gave better fits of his experimental results. The effect of initial solution pH on the adsorption of zinc by natural zeolite is shown of Fig. 6.

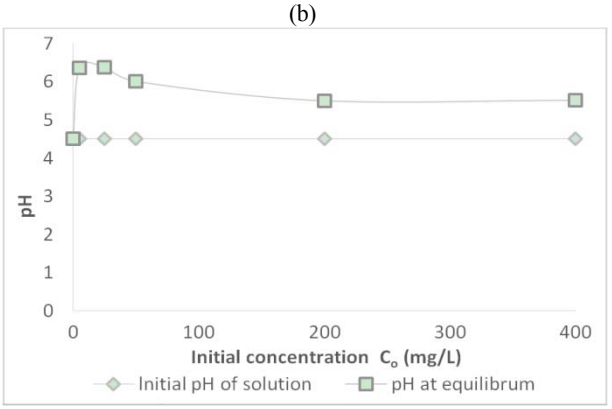
Fig. 6 presents the variation in the equilibrium pH values with respect to initial zinc concentration in each equilibrium study. The equilibrium pH values are



(a)



(b)



(c)

Fig. 6 Equilibrium pH change with respect to various initial zinc concentrations. The initial solutions where at different pH values. Error in pH reading is ±0.2. (a) Initial pH is 2.5, (b) initial pH is 3.5 and (c) initial pH is 4.5.

greater than the initially adjusted pH values and the difference between equilibrium pH and initial pH exhibits a descending trend with increasing initial zinc concentration. The increase in pH is a result of the adsorption of H^+ ions from solution, but as the initial concentration of zinc increases, the concentration driving force begins to favour the adsorption of Zn^{2+} ions in preference to H^+ ions, thus the descending trend of the equilibrium pH at higher initial zinc

concentrations. According E. Erdem natural zeolite has a buffering effect [13]. The same can be concluded from our research (Fig. 6).

The probability of zinc precipitating out of solution is very small since the equilibrium pH ranges up to 6.38, Fig. 6c, and this is lower than the minimum pH (8.4) needed for the precipitation of zinc [14].

4. Conclusions

The adsorption of zinc ions from diluted solution onto natural zeolite occurs efficiently.

Equilibrium studies show that adsorption of zinc ions strongly depends on the initial concentration and pH of solutions. As the initial concentration of zinc cations increases, the amount of metal adsorbed per gram of natural zeolite (q_e) increases, and as the solution pH increases, there is a general increase in adsorption capacity.

Langmuir isotherms for the adsorption of zinc from solution gave better fits of the experimental results than Freundlich isotherms. The applicability of the Langmuir isotherm suggests monolayer coverage of the Zn^{2+} at the surface of the natural zeolite or that a similar exchangeable ions with equivalent concentration was exchanged by Zn^{2+}. According to R_L values, adsorption for all different pH values was favourable ($0 < R_L < 1$).

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